METHYLENE CHLORIDE

Identified as a toxic air contaminant under California's air toxics program (AB 1807) in 1987.

CAS Registry Number: 75-09-2 $ClCH_2Cl$

Molecular Formula: CH_2Cl_2

Methylene chloride is a volatile, nonflammable, colorless, liquid with a sweetish chloroform-like odor. It is slightly soluble in water and miscible with alcohol, ether, and dimethylformamide (Merck, 1989). In the absence of moisture, at ordinary temperatures, methylene chloride is relatively stable. In dry air, methylene chloride decomposes at temperatures exceeding 120 °C. Methylene chloride evaporates relatively quickly from water (ARB, 1989c). Possible thermal breakdown products of methylene chloride include phosgene, chlorine, and hydrogen chloride (Olson, 1994).

Physical Properties of Methylene Chloride

Synonyms: dichloromethane; methylene dichloride; Freon 30; Aerothene NM; Somethine; methylene bichloride

Molecular Weight:	84.94
Boiling Point:	39.75 °C at 760 mm Hg
Melting Point:	-95 °C
Vapor Pressure:	349 mm Hg at 20 °C
Vapor Density:	2.93 (air = 1)
Density/Specific Gravity:	1.3255 at 20/4 °C
Log Octanol/Water Partition Coefficient:	1.30
Conversion Factor:	1 ppm = 3.47 mg/m^3

(HSDB, 1995; Merck, 1989; Sax, 1989; U.S. EPA, 1994a; U.S. EPA, 1982)

SOURCES AND EMISSIONS

A. Sources

Methylene chloride is used as a solvent, a blowing and cleaning agent in the manufacture of polyurethane foam and plastic fabrication, and in paint stripping operations. Methylene chloride is also used in some aerosol consumer products, including aerosol paints, and automotive products. However, most consumer products manufacturers have already voluntarily phased out the use of

methylene chloride. In addition, in the case of aerosol paints, the use will be restricted by a provision in the Air Resources Board's (ARB) regulation, "Regulation for Reducing Volatile Organic Compound (VOC) Emissions from Aerosol Coating Products" adopted March 1995. Methylene chloride is also found in textiles, paper, plastic, glass, and pharmaceutical manufacturing. For some categories, such as paint removers and aerosols, emissions from evaporation equal the amount used (ARB, 1989c).

Paint removers account for the largest use of methylene chloride in California, where methylene chloride is the primary ingredient in paint stripping formulations used for industrial, commercial, military, and domestic applications (ARB, 1989c).

The primary stationary sources that have reported emissions of methylene chloride in California are plastic product manufacturers, manufacturers of synthetics, and aircraft and parts manufacturing (ARB, 1997b).

Methylene chloride was registered for use as a pesticide; however as of August 1, 1990, it is no longer registered for pesticidal use in California (DPR, 1996).

B. Emissions

The total emissions of methylene chloride from stationary sources in California are estimated to be at least 6.8 million pounds per year, based on data reported under the Air Toxics “Hot Spots” Program (AB 2588) (ARB, 1997b).

C. Natural Occurrence

Methylene chloride does not occur naturally in the environment (HSDB, 1995).

AMBIENT CONCENTRATIONS

Methylene chloride is routinely monitored in California by the statewide ARB air toxics network. When methylene chloride was formally identified as a toxic air contaminant, the ARB estimated a population-weighted annual concentration of 3.85 to 8.4 micrograms per cubic meter ($\mu g/m^3$) or 1.1 to 2.4 parts per billion (ppb) (ARB, 1989c). The network's mean concentration of methylene chloride from January 1996 through December 1996 is estimated to be 2.26 $\mu g/m^3$ or 0.65 ppb (ARB, 1997c).

The United States Environmental Protection Agency (U.S. EPA) has also reported concentrations of methylene chloride from 13 study areas during 1989 to 1991. Overall range

of concentrations from these areas were from 0.28 to 492 $\mu g/m^3$ (0.08 to 140.57 ppb) with an overall mean concentration of 5.6 $\mu g/m^3$ (1.6 ppb) (U.S. EPA, 1993a).

INDOOR SOURCES AND CONCENTRATIONS

Because methylene chloride is a constituent in many consumer products, short-term indoor concentrations may be several orders of magnitude higher than ambient concentrations. Results from a chamber study where a paint stripper was being used resulted in breathing zone exposures up to 2,000 parts per million (ppm) averaged over one hour with peak breathing zone concentrations of up to 33,000 ppm. Inhalation of methylene chloride from the indoor environment is expected to vary depending on the degree and manner of use of products containing methylene chloride (Girman and Hodgson, 1986).

Data on indoor concentrations of methylene chloride are extremely limited. During June of 1990, 125 households in Woodland, California were monitored for a variety of toxic air contaminants (Sheldon et al., 1992). Sixty-one homes were sampled for methylene chloride. The mean of those samples was 83 $\mu g/m^3$ or 23.92 ppb. The detection limit for methylene chloride was 0.7 $\mu g/m^3$ or 0.20 ppb. The 90th percentile was 160 $\mu g/m^3$ or 46.11 ppb, with a range from below the quantifiable limit of 0.7 to 1,700 $\mu g/m^3$ or 0.20 to 489.91 ppb. Mean indoor concentrations are approximately 5.5 times greater than the outdoor mean concentration of 15 $\mu g/m^3$ or 4.32 ppb from the same study. The use of household consumer products containing methylene chloride may account for its high prevalence in the homes tested (ARB, 1989c).

As part of a study conducted in Los Angeles County, the indoor and outdoor air of eight homes was sampled during the summer and analyzed for several compounds including methylene chloride. For these homes, results show overnight indoor concentrations to range from 3.5 to 12.6 $\mu g/m^3$ or 0.3 to 3.6 ppb with daytime indoor concentrations ranging from 1.05 to 13.65 $\mu g/m^3$ or 0.3 to 3.9 ppb. Overnight outdoor concentrations range from 0.35 to 4.55 $\mu g/m^3$ or 0.1 to 1.3 ppb while daytime outdoor concentrations range from 0.7 to 13.65 $\mu g/m^3$ or 0.2 to 3.9 ppb. The results for this study indicate that indoor concentrations of methylene chloride in some homes may not be substantially higher than outdoor concentrations (ARB, 1989c).

ATMOSPHERIC PERSISTENCE

Reaction with hydroxyl radicals is the dominant mechanism removing methylene chloride from the atmosphere. The calculated half-life and lifetime of methylene chloride due to gas-phase reaction with the OH radical are estimated to be about 0.6 years and 0.9 years, respectively. The product of the OH radical-initiated reaction is formyl chloride, in 100 percent yield (WMOGRMP, 1995).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics "Hot Spots" Program (AB 2588). Of the risk assessments reviewed as of April 1996, methylene chloride was the major contributor to the overall cancer risk in 30 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 112 of these risk assessments. Methylene chloride also was the major contributor to the overall cancer risk in 8 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million, and contributed to the total cancer risk in 44 of these risk assessments (OEHHA, 1996a).

For non-cancer health effects, methylene chloride contributed to the total hazard index in 24 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1. Methylene chloride also contributed to the total hazard index in 30 of the approximately 107 risk assessments reporting a total acute hazard index greater than 1, and presented an individual hazard index greater than 1 in 8 of these risk assessments (OEHHA, 1996b).

HEALTH EFFECTS

The probable route of human exposure to methylene chloride is inhalation (ARB, 1989c).

Non-Cancer: Methylene chloride vapor is irritating to the eyes, respiratory tract, and skin. It is also a central nervous system depressant including decreased visual and auditory functions and may cause headache, nausea, and vomiting. At high exposures, methylene chloride can cause pulmonary edema, cardiac arrhythmias, and loss of consciousness. Chronic exposure can lead to bone marrow, hepatic, and renal toxicity. Methylene chloride is metabolized by the liver with resultant carboxyhemoglobin formation (Olson, 1994).

An acute non-cancer Reference Exposure Level (REL) of 3.5×10^3 $\mu g/m^3$ and a chronic non-cancer REL of 3.0×10^3 $\mu g/m^3$ are listed for methylene chloride in the California Air Pollution Control Officers Association Air Toxics "Hot Spots" Program, Revised 1992 Risk Assessment Guidelines. The toxicological endpoints considered for acute toxicity are the central and peripheral nervous systems, liver, and gastrointestinal system. The toxicological endpoints considered for chronic toxicity are the central nervous system, liver, and gastrointestinal system (CAPCOA, 1993). The U.S. EPA has established an oral Reference Dose (RfD) for methylene chloride of 0.06 milligrams per kilogram per day based on liver toxicity in rats, and is currently reviewing a Reference Concentration (RfC) (U.S. EPA, 1994a).

No information on adverse reproductive effects in humans from inhalation or oral exposure has been found, but fetotoxicity was observed in pregnant rodents exposed by inhalation to high

concentrations of methylene chloride throughout pregnancy as evidenced by reduced fetal body weight and reduced skeletal ossification (U.S. EPA, 1994a; ARB, 1989c).

Cancer: Methylene chloride increases tumor rates in the mouse liver and lung and the rat mammary gland at concentrations ranging from 1,000 to 4,000 ppm. The U.S. EPA has classified methylene chloride in Group B2: Probable human carcinogen with an inhalation unit risk estimate of 4.7×10^{-7} (microgram per cubic meter)$^{-1}$. The U.S. EPA estimates that if an individual were to breathe air containing methylene chloride at 2.0 $\mu g/m^3$, over a lifetime, that person theoretically would have no more than a 1 in 1 million increased chance of developing cancer (U.S. EPA, 1994a). The International Agency for Research on Cancer (IARC) has classified methylene chloride (dichloromethane) in Group 2B: Possible human carcinogen based on limited animal evidence (IARC, 1987a).

The State of California under AB 1807 and Proposition 65 listed methylene chloride (dichloromethane) as a carcinogen and as a Toxic Air Contaminant (ARB, 1989c; CCR, 1996). The inhalation potency factor that has been used as a basis for regulatory action in California is 1×10^{-6} (microgram per cubic meter)$^{-1}$ (OEHHA, 1994). In other words, the potential excess cancer risk for a person exposed over a lifetime to 1 $\mu g/m^3$ of methylene chloride is estimated to be no greater than 1 in 1 million. The oral potency factor that has been used as a basis for regulatory action in California is 1.4×10^{-2} (milligram per kilogram per day)$^{-1}$ (OEHHA, 1994).